



UNIVERSITI PUTRA MALAYSIA

**INTERACTION OF POLY(ETHYLENEGLYCOL) ETHER IN ISOTROPIC
REGION, L2, OF MIXED SODIUM DODECYL SULPHATE
(SDS) - SODIUM CAPRYLATE (SCA) SYSTEM**

LIM WEN HUEI

FSAS 1996 14

**INTERACTION OF POLY(ETHYLENE GLYCOL) ETHER IN ISOTROPIC
REGION, L_2 , OF MIXED SODIUM DODECYL SULPHATE
(SDS) - SODIUM CAPRYLATE (SCA) SYSTEM**

By

LIM WEN HUEI

**Thesis Submitted in Fulfillment of the Requirement for
the Degree of Master of Science in the Faculty of
Science and Environment Studies,
Universiti Pertanian Malaysia.**

April 1996



ACKNOWLEDGEMENTS

First of all I would like to thank God for His mercy, guidance and patience toward my spiritual growth and walk with Him in this two years. I would also like to thank my committee members, Assoc. Prof. Dr. Hamdan Suhaimi (chairman), Assoc. Prof. Dr Wan Md. Zin Wan Yunus, and Dr. Mansor Ahmad for their guidance, ideas, and time toward my project and giving me the opportunity to work independently. My gratitude to all the lecturers in the Chemistry Department for their noteworthy assistance, not forgetting En. Zainal Zahari Zakaria for running the samples.

My loving care also goes to all of my family members especially my parent for their cares and sacrifices for the sake of my success. Not forgetting to you, “dear”, for making my life more colourful. Lastly, to my friends and juniors in UPM, thank you for everything.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	iii
LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
LIST OF ABBREVIATIONS.....	xiv
ABSTRACT.....	xv
ABSTRAK.....	xvii

CHAPTER

I	INTRODUCTION.....	1
	Mixed Surfactants.....	5
	Application of Microemulsion.....	15
	Phase Equilibria.....	17
	Interaction of Surfactant-Polymer.....	18
	Instrumentation.....	23
	Objectives.....	24
II	LITERATURE REVIEW.....	26
	Surfactant-Polymer Interaction.....	26
	Nuclear Magnetic Resonance (H^1 NMR).....	29
	Rheological Characteristics of the Microstructure.....	34
III	MATERIALS AND METHODS.....	46
	Materials.....	46
	Experimental Design.....	47
	Determination of Phase Equilibria.....	48
	Nuclear Magnetic Resonance Spectroscopy (NMR).....	53
	Viscosity Measurements.....	55
IV	RESULTS AND DISCUSSIONS.....	58
	Determination of Phase Diagrams.....	58
	The Behaviour of Molecules in the W/O Isotropic Region.....	73
	Viscosity Measurements.....	111



	Page
V CONCLUSION AND FUTURE WORK.....	121
Conclusion.....	121
Future Work.....	123
BIBLIOGRAPHY.....	125
VITA.....	133

LIST OF TABLES

Table	Page
1 List of chemicals.....	46

LIST OF FIGURES

Figure		Page
1	Structures of (a) Inverse micelle, (b) w/o microemulsion and (c) w/o emulsion.....	4
2	Approximate size ranges for surfactant assemblies and related structures.....	6
3	Structure of a surfactant.....	8
4	Classification of surfactants.....	9
5	Possible states of an amphiphile in solution (Myer, 1988).....	11
6	Area per surfactant molecule at the surface of the micellar core (Tanford, 1977).....	14
7	Applications of microemulsion.....	16
8	Quarternary of a phase diagram.....	19
9	Schematic illustration of the flow pattern for (a) a pure liquid near a stationary wall and for a dispersion that contains (b) nonrotating (c) rotating particles.....	35
10	Experimental verification of Einstein's law of viscosity for spherical particals of several dfferent sizes (squares, yeast particles, $R=2.5 \mu\text{m}$; circles,fungus spores, $R=4.0 \mu\text{m}$; triangles, glass spheres, $R=80 \mu\text{m}$). Open symbols represent measurement in concentric cylinder viscometers, and close symbols measurements in capillary viscometers (Eirich <i>et al.</i> , 1936).....	37
11	Viscosity of surfactant solution at different volume fraction of water.....	39
12	Reduced viscosity versus volume fraction for a dispersion of glass spheres ($R=6.5 \times 10^{-3} \text{ cm}$) up to $\phi \cong 0.40$ (Vand, 1948)....	41

	Page
13 The orientation of an unsolvated sphere.....	44
14 (a) Intrinsic viscosity as a function of the axial ratio a/b for oblate and prolate ellipsoids of revolution according to Simha theory. (b) Experimental values of relative viscosity versus volume fraction for tobacco mosaic virus of different a/b ratio (Lauffer, 1944).....	45
15 Diagram of Experimental Design.....	47
16 Construction of phase diagram : a) Inverse micelle; b) w/o microemulsion; and c) polymer-w/o microemulsion.....	50
17 Titration paths followed in the experiments. A - surfactant mixture; B - aqueous phase; C - oil phase, starting fraction for titration; e1, e2, e3, macroscopically homogeneous solution.....	52
18 Phase equilibria at different temperatures.....	54
19 Phase diagram of pure surfactant (S) of SDS and SCA in : a) ——— SDS/ $C_6H_{13}OH/H_2O$ system and b) ——— SCA/ $C_6H_{13}OH/H_2O$ system at $25.0 \pm 0.1^\circ C$	59
20 Phase diagram of mixed surfactant (S) of SDS-SCA/ $C_6H_{13}OH/H_2O$ system with the weight ratio of SDS:SCA : a) ——— - 3:1; b) ——— - 3:2; c) ——— - 2:3 and d) - 1:3, at $25.0 \pm 0.1^\circ C$	60
21 The percentage of water intake at difference weight ratio of SDS:SCA on the lines : a) 75.0 wt% mixed surfactants and 25.0 wt% 1-hexanol; b) 77.5 wt% mixed surfactants and 22.5 wt% 1-hexanol; and c) 80.0 wt% mixed surfactants and 20.0 wt% 1-hexanol.....	62
22 Phase diagram of w/o microemulsion region :a) ——— SDS-SCA- $C_6H_{13}OH/ C_{10}H_{22}/H_2O$; b) ——— SDS- $C_6H_{13}OH/C_{10}H_{22}/H_2O$; and c) SCA- $C_6H_{13}OH/ C_{10}H_{22}/H_2O$ systems at $25.0 \pm 0.1^\circ C$	63

		Page
23	Phase diagram of SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /mPEG2,000/ H ₂ O system at 25.0 ± 0.1°C.....	64
24	Phase diagram of SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /mPEG2,000/ H ₂ O system at difference temperature : a) ——— - 20.0°C; b) - - - - 30.0°C; c) - . - . - 50.0°C; and d) - 65.0°C..	66
25	The percentage of water uptake as temperature increases from 20.0°C to 65.0°C at lines TP1 (29.0 wt% mPEG2,000 and 71.0 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂) and TP2 (3.0 wt% mPEG2,000 and 97.0 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂).....	68
26	Phase diagram of SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /PEG8,000/ H ₂ O system at 25.0 ± 0.1°C.....	69
27	Phase diagram of SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /PEG8,000/H ₂ O system at difference temperature : a) ——— - 20.0°C ; b) - - - - 30.0°C; c) - . - . - 50.0°C; and d) - 65.0°C..	71
28	The percentage of water uptake as temperature increases from 20.0°C to 65.0°C at lines TT1 (2.0 wt% PEG8,000 and 98.0 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂) and TT2 (20.0 wt% PEG8,000 and 80.0 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂).....	72
29	Phase diagram of : a) ——— SDS-SCA-C ₆ H ₁₃ OH C ₁₀ H ₂₂ /H ₂ O/mPEG2,000; b) — . — . SDS-SCA-C ₆ H ₁₃ OH C ₁₀ H ₂₂ /H ₂ O/PEG8,000 systems at 20.0 ± 0.1°C.....	74
30	Phase diagram of : a) ——— SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ / H ₂ O/mPEG2,000; b) - . - . SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /H ₂ O/ PEG8,000 systems at 30.0 ± 0.1°C.....	75
31	Phase diagram of : a) ——— SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /H ₂ O/mPEG2,000; b) — . — . SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /H ₂ O/PEG8,000 systems at 50.0 ± 0.1°C.....	76
32	Phase diagram of : a) ——— SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /H ₂ O/mPEG2,000; b) - . - . SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /H ₂ O/PEG8,000 systems at 65.0 ± 0.1°C.....	77

	Page
33 NMR spectrum of the inverse micelle of SDS-SCA/C ₆ H ₁₃ OH/H ₂ O system.....	78
34 NMR spectrum of the w/o microemulsion of SDS-SCA-C ₆ H ₁₃ OH/C ₁₀	79
35 NMR spectrum of the polymer-w/o microemulsion isotropic region of SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ /H ₂ O/mPEG2,000 system.....	80
36 NMR spectrum of the polymer-w/o microemulsion isotropic region of SDS-SCA-C ₆ H ₁₃ OH-C ₁₀	81
37 Phase diagram of SDS-SCA/C ₆ H ₁₃ OH/H ₂ O system where lines: A: 77.5 wt% mixed surfactants (SDS and SCA) and 22.5 wt% C ₆ H ₁₃ OH. B: 36.0 wt% mixed surfactants (SDS and SCA) and 64.0 wt% water.....	83
38 Chemical shift, δ of each peaks at different percentage of water along line A: 77.5 wt% mixed surfactants (SDS and SCA) and 22.5 wt% C ₆ H ₁₃ OH.....	84
39 Line width, Hz of each peaks at different percentage of water along line A: 77.5 wt% mixed surfactants (SDS and SCA) and 22.5 wt% C ₆ H ₁₃ OH.....	86
40 Chemical shift, δ of each peaks at different percentage of 1-hexanol along line B: 36.0 wt% mixed surfactants (SDS and SCA) and 64.0 wt% water.....	88
41 Line width, Hz of each peaks at different percentage of 1-hexanol along line B : 36.0 wt% mixed surfactants (SDS and SCA) and 64.0 wt% water.....	89
42 Phase diagram of w/o microemulsion region of SDS-SCA-C ₆ H ₁₃ OH/C ₁₀ H ₂₂ /H ₂ O system where : i) line E: 35.0 wt% C ₁₀ C ₆ H ₁₃ OH) ii) line F: 20.0 wt% water and 80.0 wt% (SDS-SCA-C ₆ H ₁₃ OH).....	90

	Page	
52	Phase diagram of polymer-w/o microemulsion of SDS/SCA/C ₆ H ₁₃ OH/C ₁₀ H ₂₂ /H ₂ O/PEG8,000 system where : i) line 1P8: 12.0 wt% H ₂ O and 88.0 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂ ii) line 2P8: 16.2 wt% PEG8,000 and 83.8 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂	105
53	Chemical shift, δ of polymer-w/o microemulsion region at different percentage of PEG8,000 along line 1P8 : 12.0 wt% H ₂ O and 88.0 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂	106
54	Line width, Hz of polymer-w/o microemulsion region at different percentage of PEG8,000 along line 1P8 : 12.0 wt% H ₂ O and 88.0 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂	108
55	Chemical shift, δ of polymer-w/o microemulsion region at different percentage of water along line 2P8 : 16.2 wt% PEG8,000 and 83.8 wt% SDS/SCA/C ₆ H ₁₃ OH/C ₁₀ H ₂₂	109
56	Line width, Hz of polymer-w/o microemulsion region at different percentage of PEG8,000 along line 2P8 : 16.2 wt% PEG8,000 and 83.8 wt% SDS-SCA-C ₆ H ₁₃ OH-C ₁₀ H ₂₂	110
57	Relative viscosity, η_{rel} of line A in the isotropic region as the volume fraction of water, ϕ is increased at $25.0 \pm 0.5^{\circ}\text{C}$	112
58	Relative viscosity, η_{rel} of line E in the isotropic region as the volume fraction of water, ϕ is increased at $25.0 \pm 0.5^{\circ}\text{C}$	114
59	Relative viscosity, η_{rel} of line 2P2 which consists 16.2 wt% mPEG2,000 in the isotropic region of polymer-w/o microemulsion as the volume fraction of water, ϕ is increased at $25.0 \pm 0.5^{\circ}\text{C}$	116
60	Relative viscosity, η_{rel} of line 1P2 which consists 20.0 wt% H ₂ O in the isotropic region of polymer-w/o microemulsion as mPEG2,000 is increased at $25.0 \pm 0.5^{\circ}\text{C}$	117
61	Relative viscosity, η_{rel} of line 2P8 which consists 16.2 wt% PEG8,000 in the isotropic region of polymer-w/o microemulsion as the volume fraction of water, ϕ is increased at $25.0 \pm 0.5^{\circ}\text{C}$	119

	Page
62 Relative viscosity, η_{rel} of line 2P8 which consists 12.0 wt% H ₂ O in the isotropic region of polymer-w/o microemulsion as PEG8,000 is increased at $25.0 \pm 0.5^\circ\text{C}$	120

LIST OF ABBREVIATIONS

SDS	Sodium Dodecyl Sulphate
SCA	Sodium Caprylic Acid
PEG8,000	Poly(ethylene glycol) ether
mPEG2,000	Poly(ethylene glycol) monomethoxy ether
$C_6H_{13}OH$	1-hexanol
$C_{10}H_{22}$	n-decane
w/o	water in oil
o/w	oil in water

Abstract of thesis submitted to the Senate of Universiti Pertanian Malaysia in fulfilment of the requirement for the degree of Master of Science.

INTERACTION OF POLY(ETHYLENE GLYCOL) ETHER IN ISOTROPIC REGION, L_2 , OF MIXED SODIUM DODECYL SULPHATE (SDS) - SODIUM CAPRYLATE (SCA) SYSTEM

By

LIM WEN HUEI

August 1996

Chairman : Assoc. Prof. Dr. Hamdan Suhaimi

Faculty : Science and Environmental Studies

Mixed surfactants of SDS-SCA at weight ratio of 2:3 in SDS-SCA/ $C_6H_{13}OH/H_2O$ system gives the largest inverse micelle region. This system is used for further construction of the w/o microemulsion phase diagram where n-decane is added into the system. The SDS-SCA- $C_6H_{13}OH/C_{10}H_{22}/H_2O$ system shows a larger w/o microemulsion region than the pure surfactants in surfactant/1-hexanol/n-decane/water system. Maximum water solubility is found at 65.0 weight percent of n-decane and 35.0 weight percent of SDS-SCA- $C_6H_{13}OH$. Polymers, mPEG2,000 and PEG8,000 are then added into the line above in the solution. The SDS-SCA- $C_6H_{13}OH-C_{10}H_{22}/H_2O/mPEG2,000$ system is observed to have a bigger isotropic region than the SDS-SCA- $C_6H_{13}OH-C_{10}H_{22}/H_2O/PEG8,000$ system. These two

systems are sensitive to temperature where the isotropic region change dramatically as temperature is increased.

Nuclear Magnetic Resonance (NMR) is used to detect the interaction and the degree of freedom of the molecules in the isotropic solution which consist of SDS, SCA, $C_6H_{13}OH$, $C_{10}H_{22}$ and H_2O . This instrument is able to detect the formation of the inverse micelle and the w/o microemulsion in the SDS-SCA/ $C_6H_{13}OH/H_2O$ and SDS-SCA- $C_6H_{13}OH/C_{10}H_{22}/H_2O$ systems. The only interaction between the molecules are found in the SDS-SCA- $C_6H_{13}OH-C_{10}H_{22}/H_2O/mPEG2,000$ and the SDS-SCA- $C_6H_{13}OH-C_{10}H_{22}/H_2O/PEG8,000$ systems.

The viscosity of the solution confirms that the inverse micelle and the w/o microemulsion are formed in the SDS-SCA/ $C_6H_{13}OH/H_2O$ and SDS-SCA- $C_6H_{13}OH/C_{10}H_{22}/H_2O$ systems. It is observed that the aggregations are not geometrically packed together. The presence of the polymers, mPEG2,000 and PEG8,000 in the SDS-SCA- $C_6H_{13}OH/C_{10}H_{22}/H_2O$ system can break the w/o microemulsion.

Abstrak tesis yang dikemukakan kepada Senat Universiti Pertanian Malaysia sebagai memenuhi syarat untuk Ijazah Master Sains

**KAJIAN TERHADAP INTERAKSI POLI(ETILENE GLIKOL) ETHER DI
KAWASAN ISOTROPIK, L₂, YANG MENGANDUNGI CAMPURAN
NATRIUM DODESIL SULFAT (SDS) - NATRIUM KAPRILAT (SCA)**

Oleh

LIM WEN HUEI

Ogos 1996

Pengerusi : Prof. Madya Dr. Hamdan Suhaimi

Fakulti : Sains dan Pengajian Alam Sekitar

Campuran surfaktan SDS dan SCA pada nisbah berat 2:3 dalam sistem SDS-SCA/C₆H₁₃OH/H₂O menghasilkan satu kawasan misel songsang yang luas. Nisbah berat 2:3 ini digunakan untuk kajian selanjutnya dalam penghasilan w/o mikroemulsi dengan menambah n-dekana yang bertindak sebagai minyak. Sistem SDS-SCA-C₆H₁₃OH/C₁₀H₂₂/H₂O mempunyai kawasan w/o microemulsi yang luas jika dibandingkan dengan sistem SDS-C₆H₁₃OH/C₁₀H₂₂/H₂O dan sistem SCA-C₆H₁₃OH/C₁₀H₂₂/H₂O. Kelarutan air yang maksimum didapati pada garis 65 berat peratus n-dekana and 35 berat peratus SDS-SCA-C₆H₁₃OH. Polimer iaitu mPEG2,000 dan PEG8,000 akan ditambahkan pada garis di atas. Kedua-dua sistem ini, iaitu SDS-SCA-C₆H₁₃OH-C₁₀H₂₂/H₂O/mPEG2,000 and SDS-SCA-C₆H₁₃OH-C₁₀H₂₂/H₂O/PEG8,000 sensitif terhadap suhu di mana kawasan isotropik berubah

dengan kenaikan suhu. Kawasan satu fasa bagi sistem SDS-SCA-C₆H₁₃OH-C₁₀H₂₂/H₂O/PEG8,000.

NMR digunakan untuk mengesan interaksi dan darjah kebebasan molekul dalam larutan ini yang mengandungi SDS, SCA, C₆H₁₃OH, C₁₀H₂₂ dan H₂O. Ia dapat mengesan pembentukan misel songsang dan microemulsi air dalam minyak dalam sistem SDS-SCA/C₆H₁₃OH/H₂O and sistem SDS-SCA-C₆H₁₃OH/C₁₀H₂₂ /H₂O. Sistem SDS-SCA-C₆H₁₃OH-C₁₀H₂₂/H₂O/mPEG2,000 dan sistem SDS-SCA-C₆H₁₃OH-C₁₀H₂₂ /H₂O/PEG8,000 hanya menunjukkan interaksi berlaku (tiada pembentukan misel songsang dikesan).

Kelikatan larutan menunjukkan bahawa misel songsang dan microemulsi air dalam minyak terbentuk dalam sistem SDS-SCA/C₆H₁₃OH/H₂O and sistem SDS-SCA-C₆H₁₃OH/ C₁₀H₂₂ /H₂O. Agregasi ini tidak disusun secara geometri dalam larutan tersebut. Kehadiran polimer iaitu mPEG2,000 dan PEG8,000 dalam sistem SDS-SCA-C₆H₁₃OH/C₁₀H₂₂/H₂O didapati memecahkan microemulsi air dalam minyak dalam larutan.

CHAPTER I

INTRODUCTION

If two immiscible liquids (usually water and oil) are shaken together, they will naturally separate spontaneously into two distinct layers. Suppose instead of merely shaking the two liquids together, a surfactant which often called an emulsifying agent is added into it (Tadros, 1984; Rosen, 1978). The compounds are vigorously mix in a homogeniser, then the milling together of the constituents causes one to be dispersed (the inner phase) in the other (the continuous phase), where an emulsion is produced (Becher, 1983; Vold and Vold, 1983; Shinoda and Friberg, 1986; Florence and Whitehill, 1982). This macroemulsion may be kinetically stable for a long period of time, but in the end, it will suffer the same fate as above, which is phase separation, in order to attain a minimum interfacial free energy (although effort can be made to decrease kinetic rate constants but the thermodynamic drive force remains unchanged, that is to minimise the interfacial area of contact between immiscible phase). A transparent or slightly bluish solution (because these particles are much smaller than the wavelength of visible light) is formed when a suitable composition of the system (contains surfactant, co-surfactant or oil and water) is reached.

This so-called microemulsion is formed when the chemical systems containing oil, water or an aqueous salt solution, surfactant and sometimes a co-surfactant such as alcohol (of an intermediate chain length) are mixed together (Prince, 1977; Mittal, 1976; Elworthy *et al.*, 1968; Schulman *et al.*, 1959; Bourrel and Szlechter, 1988). It appear to be thermodynamically stable compositions and it has an essentially infinite lifetime, assuming that there are no changes in such factors as composition, temperature, and pressure (Overbeek, 1978; Adamson, 1969; Van Vourst Vader, 1960).

The question is, does this transparent solution contain microemulsions or micelles? Micelles do exist in clear solutions too (Elworthy *et al.*, 1968; Rosen, 1978; Mittal, 1979). When one compares microemulsions and micelles, the demarcation line can become quite blurred and, in some it does not even exist. Clearly there is some disagreement as to the true definition of clear isotropic solution as microemulsions [where some prefer the names “swollen micelles solutions” or “solubilised micellar solutions”] or micelles (Winsor, 1948). Some distinguish these microemulsions and micelles solutions by the degree of arbitrariness, especially in view of the continuity, that one observes in the physical properties such as the increased of solubility. One possible definition is to assert that a microemulsion is composed of bulk isotropic oil and water regions separated by an anisotropic layer. The interior of a micelle, the oil region, is composed entirely of the lipophilic portions of the amphiphile and is probably not isotropic. But even a micelle containing a small quantity of solubilise has an isotropic interior. However, as the amounts of oil and water in the micellar solution both become large and approximately of the same volume, it would be

anticipated that bulk isotropic oil and water regions would essentially at some point both exist. However, a microemulsion is thought to be distinct and separate from a micellar solution even though there is no existing technique to distinguish between these two states of matter.

Figure 1 shows the difference between inverse micelle, w/o microemulsion and w/o emulsion. The term microemulsion was coined in 1958 by Schulman and workers to describe a fairly specific class of colloidal system (Schulman *et al.*, 1959). Various experimental approaches have been used in an attempt to ascertain all of the details of their thermodynamic and structural characteristics (Prince, 1977; Mittal, 1976; Bourrel and Szlechter, 1988). It was found that this transparent or translucent system formed spontaneously when oil and water were mixed with relatively large amounts of combined surfactant with co-surfactant. As a result, new theories of the formation and stability of these complex systems were developed, depend on their preparation and the relationships among the chemical structure of the oil phase, the compositions of the aqueous phase, and the structure of the surfactant and co-surfactant (Bourrel and Szlechter, 1988).

A microemulsion normally has droplet diameters of 100 nm or less (up to 5 nm). It is slightly larger than micellar systems because microemulsion is much smaller than the wavelength of visible light. The formation of a microemulsion must have a very specific compositions and chemical structures of various components, that the nomenclature for this separate class of dispersed species has developed. Many

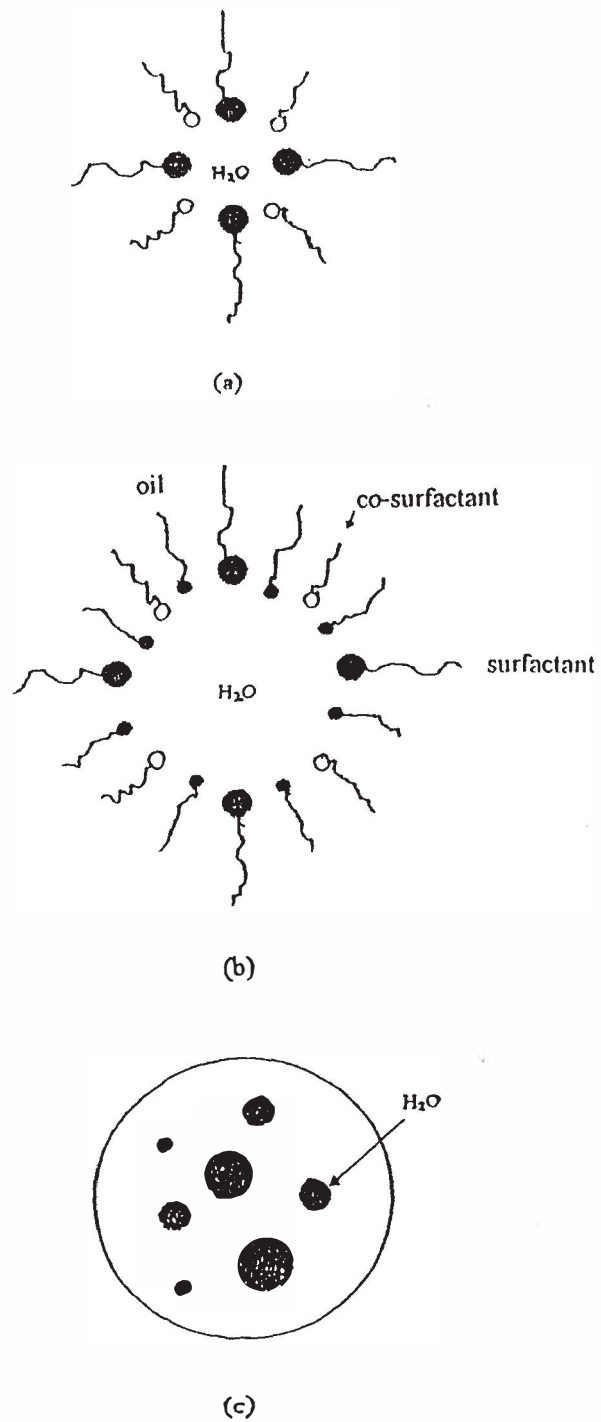


Figure 1: Structures of (a) Inverse micelle (b) w/o microemulsion and (c) w/o emulsion.

microemulsion systems have been described in which the dispersed phase to surfactant (and co-surfactant) ratio exceeds 100, and the high additive to surfactant ratio requires that there be a core of dispersed material that is essential to the bulk phase of the additive (Tadros, 1984). Therefore continuous transitions occur from molecular solution via swollen micelles (or inverse micelle) to microemulsion where the transition from swollen micelles to microemulsions can only be located arbitrarily at a radius of the order of 3 nm.

If one constructs a spectrum of the possible situations for the dispersion of one liquid phase in another, oil in water (o/w), for instance, the possible sizes of the dispersed phase units range from the molecular dispersed solution where “droplet” sizes are on the order of a few nanometers to macroemulsion with droplets of hundreds or thousands of nanometers, as shown in Figure 2. These classifications as shown are certainly arbitrary in their ranges and some overlap inevitably occurs.

Mixed Surfactants

All in all, the formation of micelle or inverse micelle to w/o (water in oil) or o/w (oil in water) microemulsion and emulsion (whether w/o or w/o) is due to the presence of an active compound namely surfactant (Ottewil, 1983). A surfactant or surface active agent, is a substance that when present at low concentration in a system has the property of absorbing onto the surfaces or the interfaces of the system, and thus altering to a marked degree of the surface (or interface) free

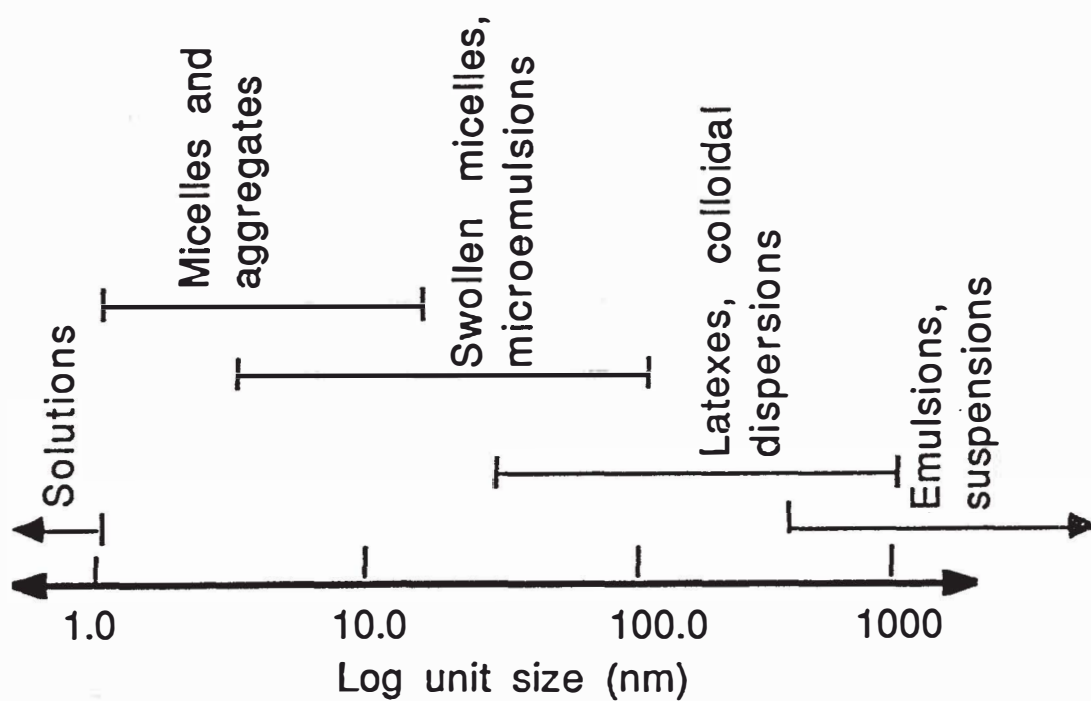


Figure 2 : Approximate size ranges for surfactant assemblies and related structures.

energies of those surfaces or interfaces (Arthur, 1990). It also can be defined as a group of chemical compounds, which usually constitute a hydrocarbon portion and a polar or ionic portion (Benson, 1967; Lucassen, 1981) as illustrated in Figure 3. The term interface denotes a boundary between any two insoluble (or immiscible) phases, the term surface indicates an interface where one phase is a gas, usually air.

In terms of classification, surface active agents are categorised into four types, depending on the nature of the head group. They are cationic, anionic, nonionic and zwitterionic, as shown in Figure 4. Due to their amphiphatic structure, surfactants absorb strongly onto the surface or the interface of air/water or oil/water systems thus altering the properties of these surface or interface. The hydrocarbon portion (tail) or lyophobic group, which can be linear or branched interacts very weakly with the solvent (aqueous solution) molecules in the aqueous environment. The strong interactions of the head group with the solvent is called the lyophilic group. When a surface active agent is dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent will cause a distortion of the solvent liquid structure (the molecules at a surface have higher potential energies than those in the interior). This is because of the stronger interaction with the molecules in the interior of the substance than the widely spaced gas molecules above it, increasing the free energy of the system.